

Quantum and thermal phase transitions in the Bechgaard salts and their analogs

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In order to investigate quantum and thermal phase transitions in the Bechgaard salts and their sulfur analogs, we perform finite-temperature Hartree-Fock calculations in one dimension with particular emphasis on the interplay between charge ordering and lattice instability. The coexisting charge- and spin-density-wave state as well as its precursor fluctuations in $(\text{TMTSF})_2\text{PF}_6$ and the lattice tetramerization in $(\text{TMTTF})_2\text{ReO}_4$ are well interpreted.

Keywords: Equilibrium thermodynamics and statistical mechanics, Order-disorder phase transitions, Organic conductors based on radical cation and/or anion salts

The Bechgaard salts $(\text{TMTSF})_2X$ and their sulfur analogs $(\text{TMTTF})_2X$, where $X = \text{PF}_6, \text{ReO}_4, \text{Br}$, etc., exhibit various types of charge and/or spin ordering [1] and stimulate our interest in quasi-one-dimensional correlated electron systems with a three-quarter-filled (quarter-filled in terms of holes) π band. A variety of mechanisms have been proposed in an attempt to interpret the variety of instabilities, featuring dimensionality [2–6], which can be tuned by pressure as well as chemically, intrachain dimerization [6–9] due to the anion columns, and competing Coulomb interactions [7,8,10,11]—on-site, nearest-neighbor, and even next-nearest-neighbor repulsions. Recently, introducing another interesting viewpoint—the interplay between charge ordering and lattice instability, several authors [2,5,6] have revealed further exotic density-wave states. In particular, Riera and Poilblanc [5,6] found charge-density-wave (CDW)-bond-order-wave (BOW) mixed phases of new type, which consist of the superposition of lattice dimerization and tetramerization, and pointed out their relevance to the spin-Peierls transition [12] recently observed in TMTTF salts.

Thus motivated, we explore thermal, as well as quantum, phase transitions in the Bechgaard-Fabre salts taking account of long-range Coulomb and electron-lattice interactions. We consider a one-dimensional model at quarter filling,

$$\mathcal{H} = \mathcal{H}_T + \mathcal{H}_U + \mathcal{H}_V + \mathcal{H}_{V'} + \mathcal{H}_K, \quad (1)$$

where

$$\begin{aligned} \mathcal{H}_T &= \sum_{j,\sigma} \left(t_j c_{j,\sigma}^\dagger c_{j+1,\sigma} + \text{H.c.} \right), \\ \mathcal{H}_U &= U \sum_j n_{j,\uparrow} n_{j,\downarrow}, \\ \mathcal{H}_V &= \sum_j V_j n_j n_{j+1}, \quad \mathcal{H}_{V'} = V' \sum_j n_j n_{j+2}, \\ \mathcal{H}_K &= \frac{1}{2} \sum_j K_j (u_{j+1} - u_j)^2, \end{aligned} \quad (2)$$

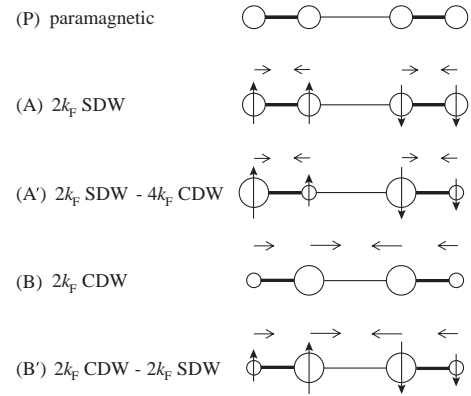


FIG. 1. Schematic of various spin-charge-lattice instabilities, where the various circles, segments, and vertical arrows qualitatively describe the variation of charge densities, bond orders, and spin densities, respectively, while the horizontal arrows denote lattice distortion from equilibrium.

with $c_{j,\sigma}^\dagger$ creating a hole of spin σ on the j th molecular site, u_j being the displacement of the j th molecular site from equilibrium, $n_{j,\sigma} = c_{j,\sigma}^\dagger c_{j,\sigma}$, and $n_j = n_{j,\uparrow} + n_{j,\downarrow}$. Considering the intrinsic dimerization of the system due to the anion columns, we introduce alternation to transfer integrals, nearest-neighbor Coulomb interactions, and spring constants as $t_j = -t_\lambda + \alpha_\lambda(u_{j+1} - u_j)$, $V_j = V_\lambda$, and $K_j = K_\lambda$, where λ is set to “a” for an odd j and to “b” for an even j . We calculate the free energy within the Hartree-Fock approximation, which should be distinguished from the mean-field treatment of the Hartree level [3,7,9,10] and is crucially superior to it with intersite Coulomb interactions included. The lattice distortion is adiabatically treated and can therefore be described in terms of the electron density matrices. We always set the smaller ones of the intrinsic transfer integrals and the spring constants, t_b and K_b , both equal to unity. The Hamiltonian (1) possesses various density-wave solutions, some of which are schematically shown in Fig. ??, where (A), (A’), and (B’) are accompanied by spin alignment and their nonlocal stabilization into a spin density wave (SDW) assumes weak interchain interaction.

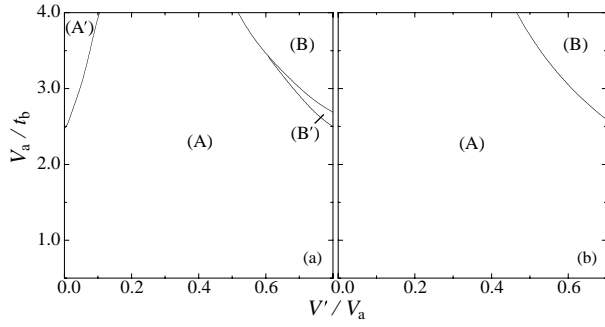


FIG. 2. Ground-state phase diagrams: (a) $t_a/t_b = 1.1$, $U/t_b = 4.0$, $V_b/V_a = 0.8$, $\alpha_a/(t_b K_a)^{1/2} = 0.1$, $\alpha_b/(t_b K_b)^{1/2} = 0.11$, $K_a/K_b = 1.1$; (b) $t_a/t_b = 1.35$, $U/t_b = 4.0$, $V_b/V_a = 0.7$, $\alpha_a/(t_b K_a)^{1/2} = 0.5$, $\alpha_b/(t_b K_b)^{1/2} = 0.6$, $K_a/K_b = 1.2$.

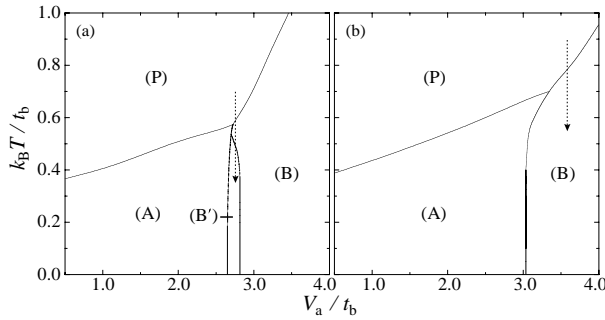


FIG. 3. Thermal phase diagrams on the lines of $V'/V_a = 0.75$ in Fig. 2(a) and of $V'/V_a = 0.6$ in Fig. 2(b), where the dotted arrows imply the thermal behaviors observed in $(\text{TMTSF})_2\text{PF}_6$ (a) and in $(\text{TMTTF})_2\text{ReO}_4$ (b), respectively.

We show in Fig. 2 ground-state phase diagrams calculated for typical parameters [9,10] of $(\text{TMTSF})_2\text{PF}_6$ (a) and for those [1,13] of $(\text{TMTTF})_2\text{ReO}_4$ (b). The intrinsic dimerization (bond alternation) is more remarkable in TMTTF salts than in TMTSF salts in general. Figure 2(a) may be compared with a pioneering calculation by Kobayashi *et al.* [10], which was carried out within the Hartree approximation under frozen lattice. The two calculations are qualitatively alike, but the long-range Coulomb effect of the Fock field on magnetic phases strongly reduce the coexisting CDW and SDW phases (A') and (B').

Taking account of experimental observations [1,13], we focus on particular regions in Fig. 2 and show their thermal behaviors in Fig. 3. In $(\text{TMTSF})_2\text{PF}_6$, a precursor CDW fluctuation of type (B) comes at about 150 K, it is reduced and a SDW fluctuation of type (A) grows instead at about 50 K, and then the mixed state (B') is stabilized below 12 K. Figure 3(a) well solves these observations. Any transition to (B'), whether from (A) or from (B),

is of second order, whereas transitions between (A) and (B) are of first order. Therefore, the $2k_F$ CDW and SDW fluctuations may in principle coexist in the intermediate temperature region. It is true that we narrowly find such a multistep thermal behavior within the present model, but we could ensure the possibility by including the crucial effect of the anion potential [6]. In $(\text{TMTTF})_2\text{ReO}_4$, on the other hand, the lattice-tetramerized CDW state (B) is stabilized below about 160 K. There is neither precursor SDW fluctuation at intermediate temperatures nor static spin ordering at low temperatures. Figure 3(b) can qualitatively interpret all these observations. Applying pressure, or equivalently reducing bond alternation by chemical tuning of materials, Chow *et al.* [12] observed crossover from spin-Peierls disordered states to $2k_F$ SDW states in the Bechgaard-Fabre salts. Considering that in the $2k_F$ CDW state (B) electrons become more and more bound in singlet pairs on next-nearest-neighbor bonds with decreasing temperature and therefore the state (B) is a fair realization of the observed spin-Peierls phase, Figs. 3(a) and 3(b) are widely consistent with experiments, giving a hint in assigning parameters to the materials.

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